

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



10/528760



(43) International Publication Date
15 April 2004 (15.04.2004)

PCT

(10) International Publication Number
WO 2004/031249 A1

- (51) International Patent Classification⁷: C08F 8/32
- (21) International Application Number: PCT/FI2003/000731
- (22) International Filing Date: 6 October 2003 (06.10.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
- | | | |
|------------|-----------------------------|----|
| 02079406.1 | 4 October 2002 (04.10.2002) | EP |
| 02079173.7 | 4 October 2002 (04.10.2002) | EP |
| 03075632.4 | 4 March 2003 (04.03.2003) | EP |
| 03447092.2 | 15 April 2003 (15.04.2003) | EP |
- (71) Applicant (for all designated States except US): RAISIO CHEMICALS LTD [FI/FI]; Raisionkaari 60, FIN-21200 Raisio (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): ABBEELE VAN DEN, Henk, Jan, Frans [BE/BE]; Zelemseweg 66, B-3290 Schaffen-Diest (BE). FRIEDERICH, Joseph, Petronella [NL/NL]; Hofstraat 20, NL-6019 CC Wessem (NL). LUTTIKHEDDE, Hendrik, Jan, Gerrit [NL/FI]; Intolantie 9, FIN-21260 Raisio (FI).
- (74) Agent: OY JALO ANT-WUORINEN AB; Iso Roobertinkatu 4-6 A, FIN-00120 Helsinki (FI).
- (81) Designated States (*national*): AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, EG, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT (utility model), PT, RO, RU, SC, SD, SE, SG, SK (utility model), SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: AQUEOUS POLYMER DISPERSION, PREPARATION AND USE THEREOF

(57) Abstract: The present invention relates to an aqueous polymer dispersion comprising a copolymer of anhydride monomer units and vinyl monomer units, which copolymer has been subjected to an imidization reaction. The present invention further relates to a method for the production and use of such a dispersion.

WO 2004/031249 A1

Aqueous polymer dispersion, preparation and use thereof

The present invention relates to an aqueous polymer dispersion comprising a copolymer of anhydride monomer units and vinyl monomer units, which copolymer
5 has been subjected to an imidization reaction. The present invention further relates to a method for the production and use of such dispersion.

From EP-A-1060197 a method is known for the production of an aqueous dispersion of a styrene maleic anhydride copolymer (abbreviated generally as
10 SMA) which is partly imidized resulting in a poly(styrene-co-maleimide) [SMI] dispersion, to be used as a paper sizing composition. The dispersion is applied in a top coat to a paper surface, with the aim of reducing the water-absorption properties of the paper surface and of providing good ink-jet printing properties. According to EP-A-1060197, the copolymer is synthesised using generally known
15 processes. The copolymer is subjected to an imidization reaction, by contacting it with an aqueous solution of NH_3 or an amine (RNH_2), at a temperature of at least 95°C and a pressure which is chosen such as to avoid boiling of the reaction mixture. The molar ratio of maleic anhydride monomer units and NH_3 or amine is selected between 1:0.8 and 1:5. The imidization reaction is continued until a
20 degree of imidization of the maleic anhydride monomer units is obtained of at most 75%. Thereafter, the dispersion is applied in a top coat to the paper and the paper is dried and calendared. It has, however, been found that when printing a paper with the aqueous copolymer dispersion in the top coat disclosed in EP-A-1060197, the quality of the printing is insufficient. In particular, characters are printed
25 insufficiently sharp; the delimitation of different colours is insufficient as a consequence of which colours fade into each other.

EP-A-1060197 also includes a comparative example of a polymer dispersion prepared according to DE-A-1720746. DE-A-1720746 describes an aqueous
30 dispersion of a polymer obtained by subjecting an SMA containing about equal molar amounts of maleic anhydride and styrene to an imidization reaction in an aqueous solution of NH_3 at a temperature above 120°C . The degree of imidization in the examples is not revealed. In the comparative example of EP-A-1060197 made according to DE-A-1720746, the SMA is 89 % imidized. It has been

observed that this dispersion has a very wide particle size distribution and forms an unstable dispersion, forming a sediment already after standing for a short period.

- 5 There is thus a need for a new polymer dispersion composition with which an improved printing quality may be achieved.

There is further a need for a process of producing such an polymer dispersion composition.

10

Therefore, the present invention aims at providing an aqueous polymer dispersion composition for use in a top coat for paper, with which an improved printing of the paper may be achieved.

15

This aim is achieved with the present invention, with the technical features of the characterising part of the independent claims.

- 20 The aqueous polymer dispersion of this invention comprises a copolymer of anhydride monomer units and vinyl monomer units, of which copolymer at least 90 % of the moles of the anhydride monomer units are imidized. This polymer dispersion contains SMI in the form of discrete particles which can be called organic pigment.

- 25 Suitable anhydride monomers for use in the copolymer are, for example, α - β -unsaturated dicarboxylic anhydrides such as maleic anhydride, fumaric anhydride, citraconic anhydride, itaconic anhydride and mixtures thereof. Preferably the copolymer contains maleic anhydride monomer units.

- 30 Suitable vinyl monomers for use in the copolymer include vinyl aromatic monomers (such as styrene, α -methyl styrene, vinyl toluene and indene), mono-olefinic unsaturated hydrocarbons (such as ethylene, propylene and isobutylene), α - β -unsaturated carboxylic esters (such as acrylate esters (like ethylacrylate, butylacrylate and 2-ethylhexylacrylate), methacrylate esters (like methylmethacrylate, ethylmethacrylate and 2-hydroxyethylmethacrylate) and

maleate diesters (like dioctylmaleate)), halogenated olefins (such as vinyl chloride and vinylidene chloride) and mixtures thereof. Preferably the copolymer contains readily commercially available styrene or α -methyl styrene, although the presence of styrene monomer units is most preferred.

5

It has been surprisingly found that when using a polymer dispersion in which at least 90 mole % of the anhydride monomer units have been imidized, a coating composition is obtained which, when applied in a coating to a surface, gives an improved coating. It has been found that if the imidization degree of the copolymer is at least 90 %, the particles have a glass transition temperature (T_g) of at least 160°C and an improved mechanical strength. As a result of the improved mechanical strength the particles are capable of withstanding deformation forces occurring in the course of the calendaring process used after applying the coating to the paper surface. When applying the polymer dispersion of this invention to a paper surface, a coating is obtained which consists of a plurality of small, discrete pigment particles showing good adhesion to each other and to the surface to be coated. It has further been found that upon printing a paper surface that has been coated with the aqueous polymer dispersion of this invention, an improved printing quality may be achieved: the characters being well delimited from each other, superimposed successively applied printing layers being well delimited from each other, fading of adjacent characters and colours into each other being limited.

The observation of the improved printing quality is attributed to the fact that the coating is built up of a plurality of discrete particles, drainage channels being formed between the particles, the presence of these drainage channels taking care of fast removal of ink solvent. When analysing the problems occurring with the state of the art coatings, it has been observed that application of the coating has the effect that in the course of the calendaring the partially imidized SMI copolymer particles disintegrate, flow together and form a film. Film formation has the effect that upon printing, the removal of solvent or dispersing agent for the ink is retarded and the printing quality is adversely affected. The organic pigment dispersion coating of the present invention to the contrary shows no tendency to film formation when applied in a coating, or during calendaring.

Preferably use is made of a copolymer in which the anhydride monomer content ranges between 5-50 mole %, more preferably between 5 and 43 mole %, even more preferably between 5-36 mole % and most preferably 5-29 mole %, because of the end product properties.

5

The anhydride monomer content of 15-29 mole % is particularly preferred, as in this range the copolymer shows suitable water solubility, giving optimum imidization yield and high solid content of the final dispersion. It has been surprisingly found that the anhydride monomer content further determines the particle size, the particle size increasing with increasing anhydride monomer content, as well as the hardness of the copolymer. The properties of the copolymer particles after imidization are determined not only by the composition of the starting material, but also by the physical conditions prevailing in the imidization reaction, e.g. concentration and agitation.

15

The vinyl monomer content of the copolymer ranges between 95-50 mole %, preferably between 95-81 mole %.

20

The aqueous polymer dispersion of this invention preferably has a solid content of more than 20 wt. %, more than 30 wt. % or even more than 40 wt. %. The dispersion comprises discrete particles having a particle diameter above 30 nm, sometimes above 40 or 50 nm, but smaller than 400 nm, often smaller than 250 or even 120 nm, the particle size distribution being narrow. As the diameter of the particles is smaller than the wavelength of visible light, a smooth, high gloss and transparent coating may be obtained. By controlling the particle size, preference may be given to a coating with a higher or lower gloss, being more transparent or showing some opaqueness. The formation of small particles further entails the advantage that stabilisation of the dispersion can be dispensed with. This is in contrast to a dispersion containing larger particles which needs the presence of an emulsifier to attain a stable dispersion.

30

The present invention also relates to a process for the production of the above described aqueous polymer dispersion. According to this process an aqueous polymer dispersion is prepared by

- 1) reacting a starting copolymer of anhydride monomer units (preferably maleic anhydride) and vinyl monomer units (preferably styrene) with an aqueous solution of NH_3 or an amine (RNH_2),

5

- 2) subjecting the thus obtained reaction mixture to an imidization reaction until at least 90 mole % of the anhydride monomer units have been imidized.

To obtain a dispersion the particles of which have a T_g that is as high as possible, the imidization reaction is preferably continued until at least 95 mole %, or even virtually all anhydride monomer units have been imidized.

A copolymer containing vinyl monomer units and anhydride monomer units may be synthesised according to processes well known to the man skilled in the art, such as for example the process described in Hanson and Zimmerman, Ind. Eng. Chem. Vol. 49, nr. 11 (1957), p. 1803-1807.

In the method of this invention, the copolymer is reacted in water, an emulsifier optionally being present. To this mixture an aqueous solution of NH_3 or an amine RNH_2 is added, in which R may be an alkyl group having between 1-18 carbon atoms or an aryl group. It is however preferred to use NH_3 , although butylamine and stearylamine also appear to be suitable imidization reactants.

It is preferred to keep the excess of NH_3 or RNH_2 in the course of the imidization reaction as low as possible. To minimise the unnecessary loss of chemicals it is preferred that the molar ratio between the amine or NH_3 and the anhydride monomer in the copolymer to be imidized ranges between 0.8:1 and 1.2:1, but is preferably an equimolar ratio or slightly less. In the latter case, complete conversion of the reaction gives an odourless dispersion as all amine or NH_3 is consumed.

However, it is technically possible to choose the amount of NH_3 or RNH_2 such that the upper limit of the molar ratio of (NH_3 or RNH_2) : (anhydride monomer present

in the copolymer to be subjected to imidization) is 10:1. The lower limit may be 0.5:1. Of course it is technically feasible to keep the ratio close to equimolar ratio.

5 If so desired, the imidization reaction may be carried out in the presence of an alkali salt of an acid functional polymer containing acid functional monomer units and vinyl aromatic monomer units. For example alkali salt of styrene maleic anhydride copolymer may be used, which preferably has molecular mass of from 500 to 10000 g/mol and with maleic anhydride content of at least 30 mole %. The alkali salt may function as an emulsifying agent.

10 The anhydride monomer/vinyl monomer copolymer has a molecular weight which preferably is not too high and neither too low so as to allow obtaining a dispersion with a sufficiently high solid content. In the present invention, the anhydride monomer/vinyl monomer copolymer has a molecular weight which is at least 1000 g/mole, preferably at least 10000 g/mole, more preferably at least 60000 g/mole. 15 The molecular weight of this copolymer is preferably less than 500000, more preferably less than 200000 g/mole or less than 150000 g/mole. Ideally, the molecular weight of the starting copolymer is between approximately 50000 and 80000 g/mole as it allows obtaining so-called monodisperse dispersion with a 20 narrow particle size distribution of between 50 and 100 nm, the mean particle diameter being approximately 70 nm. Ultimately such dispersion allows obtaining a coating with an optimum gloss.

25 If so desired, the anhydride monomer/vinyl aromatic monomer copolymer used may be a copolymer composition comprising a plurality of copolymers having varying molecular weights. This function may be fulfilled by the emulsifier. The molecular weight of the copolymer after imidization has been found to be a key parameter when processing it.

30 A too high molecular weight of the copolymer involves the risk that the viscosity of the dispersion becomes too high and the solid content too low. A too low molecular weight of the copolymer involves the risk that the solid content of the dispersion gets too high, which has an adverse effect on the applicability of the dispersion. A too low molecular weight of the copolymer involves the additional

risk to intra-particle adhesion and agglomeration, due to Van der Waals attraction between the particles, involving entanglement and the formation of particles with too large dimensions.

5 In the method of this invention, the imidization reaction will mostly be carried out at a temperature above 100°C, preferably between 120-195°C, more preferably at a temperature between 130-180°C, or even 150-175°C. Below 100°C insufficient imidization has been observed. At a temperature above 170°C and in particular above 195°C, there is an increasing risk to agglomeration of the polymer, as a
10 consequence of which particle formation in the dispersion is counteracted, giving particles with a too large size which are visible when applied as a coating and easily involve film formation. Within the claimed temperature ranges, the imidization reaction is favoured over the formation of an imine-amine compound. The temperature range of 130-180°C is preferred as within this range a well-
15 defined dispersion with respect to Tg and mechanical properties and composition is obtained and the process showing good reproducibility.

Also, within the claimed temperature ranges sufficient imidization can be obtained within an economically feasible reaction time, at a pressure which is not too high,
20 e.g. approximately 7 bar. The risk to formation of imine-amine compounds should be minimised as these compounds have a lower glass transition temperature (Tg), thus giving rise to particles that are liable to film-formation in the course of a calendaring process.

25 To minimise adhesion of the reaction mixture to the reactor wall in the course of the imidization reaction, the reaction mixture is stirred. It has namely been found that after the aqueous solution of the copolymer has been contacted with ammonia or the amine, in the course of the imidization reaction a gel phase is formed, which may be broken or cut through stirring, adhesion to the reactor wall thereby being
30 minimised. This cutting action assists in shaping the particles of the dispersion formed following imidization.

The rotation speed applied upon stirring of the reaction mixture and the time during which the reaction mixture is stirred, will be in general adapted by the man

skilled in the art. Adapting this parameter allow controlling the physical properties and particle size of the dispersion obtained, i.e. allows controlling whether small particles with a smooth surface are formed which ultimately give a coating with a high gloss and good transparency, or larger particles if a more opaque coating is aimed at. Stirring assists in avoiding the formation of particles with a rough surface and non-uniform shape which, when applied as a coating would give undesired scattering. It has been observed that the more uniform the shape of the particles, the better the gloss of the coating and the better the drainage properties of the coating when imprinted. The shape of the particles is determined by forces prevailing in the course of the imidization reaction, and e.g. by the time the reaction mixture is stirred.

If so required, the imidization reaction may be carried out in the presence of an anti-foaming agent and/or an emulsifier. Suitable emulsifiers may be anionic or nonionic surfactants.

With the above described production process, an aqueous dispersion of the imidized organic pigment may be obtained with the above-described solid content and particle size.

If desired, the solid content of the dispersion may be increased by methods known by man skilled in the art, especially suitable are evaporation and ultra filtration.

When applied to a surface on top of one or more already existing coatings, due to their small size, the particles of the dispersion of this invention are capable of filling gaps left in the already applied coating. In that way a surface may be obtained which is covered by an optimum coating, providing optimum drainage properties that are hardly disturbed by the underlying coatings.

As the size of the individual particles is relatively small, a dense packing of the particles is obtained when the dispersion is applied to a surface to be coated, and dried. The small size of the particles facilitates solvent release and drying of the coating, thus minimising the risk to crack formation upon drying of the coating and improving drying time of the coating. The formation of small pigment particles

further has the advantage that inter-particle attraction is governed by Van der Waals forces, giving strong inter-particle adhesion and good adhesion to the surface to be coated. Due to the dense packing, a closed top coating is achieved which when imprinted shows good drainage properties thus providing quick drying of the ink, even after for example a coated paper has been subjected to a calendaring process. This is attributed to the formation of drainage channels upon drying of the coating. The dense coating assists in minimising penetration of ink particles to underlying coatings, as a consequence of which the sharpness and fineness with which the coated material is imprinted, thus the over-all printing quality, is improved as compared to prior art coatings. Furthermore, tearing of paper coated with the coating composition of this invention and the occurrence of wet pick is decreased.

It has been further found that with the method of this invention, the imidized pigment particles obtained are microporous. As the dimensions of the micropores are small, penetration of ink particles into the pigment particles is inhibited, as a consequence of which the printing quality of a surface coated with a coating containing the dispersion of this invention, is further improved.

The present invention further relates to a coating composition for a surface to be coated, the coating composition comprising an amount of the aqueous dispersion of this invention. The amount of organic pigment incorporated may vary within wide ranges and will mostly be determined by the application. In case of cheap paper applications, low amounts of organic pigments will be used so as to obtain a low density coating. When using a dispersion with a high concentration of organic pigment, either a more dense coating may be obtained, or the amount of dispersion used may be decreased.

The coating composition may further comprise the usual ingredients, such as binders (starch, latex, polyvinylalcohol, etc) and conventional pigments (kaolin, PCC, GCC, talc, silica, etc), which may be partly substituted by the polymer dispersion of this invention if so desired. The coating composition may further contain thickening agents. Hyperbranched polyesteramides such as those

disclosed in US 6392006 may be added to control the viscosity of the coating composition.

5 It has been found that the aqueous polymer dispersion of the present invention is a suitable coating material for a wide variety of surfaces that are to be imprinted. For example, the aqueous dispersion of this invention appears suitable for coating paper, paperboard, cardboard, an organic film (for example a polyethylene film), a metal foil, a textile sheet, etc. When coated with a coating comprising the aqueous polymer dispersion of this invention, an increased gloss of coated paper of 5-10
10 points after calendaring has been observed. This gloss improvement may be further increased by using a coating which exclusively consists of the dispersion of this invention.

15 The extent to which the anhydride monomer/vinyl monomer copolymer has been imidized determines the acidity of the imidized copolymer. Controlling the pH allows controlling foam formation in the course of the coating process. This is an advantage as compared to known coating compositions as they often contain calcium carbonate showing superfluous foaming. The pH further determines the area in which the dispersion of this invention may be applied. The dispersion of
20 this invention has been found to have a pH close to 7.

Examples

25 Characterisation methods:

PCS measurements

The average hydrodynamic radius of the particles of the dispersion after imidization was determined using Photon Correlation Spectroscopy.
30 Measurements were carried out using an ALV Laser of the Vertriebsgesellschaft mbH, Langen, Germany.

Solid content.

The solid content was determined using an infrared instrument, type Mettler LP16/PM600.

pH measurements.

5

The pH value of each sample was measured with a Knick 752 Cl, nr. 051489 pH measurement instrument.

Determining the degree of imidization.

10

The degree of imidization may for example be determined with Raman FTIR spectroscopy, by correlating the absorption intensity to the intensity of the absorption at the same wavelength of a completely imidized and a non-imidized reference sample. Before carrying out any calculations, the Raman-FTIR signals were normalised based on the absorption signals originating from the aromatic rings in the polymer chains. The calculations were based on the following absorptions:

15

20

C=O imide absorption band, relatively intense signal at approximately 1768 cm^{-1}
C=O anhydride absorption band, at approximately 1860 cm^{-1}
C=O relatively weak absorption band of carboxylic acid groups, at approximately 1715 cm^{-1}

25

30

As a reference use was made of (1) an aqueous ammonia solution of an imide free polymer, prepared starting from 26 mole % of maleic anhydride (MA) and 74 mole % of styrene, a NH_3 :maleic anhydride ratio of 3:1, at 50°C ; (2) a SMA powder that had been subjected to an imidization reaction by mixing 2 g of SMA (28 wt. % of MA, 72 wt. % of styrene; molecular weight 110000 g/mole) with 0.50 g of ureum in a double vice mini extruder, at 240°C for 5 minutes at a rotation speed of 100 rpm.

Contact angle measurements

Contact angles were measured with a contact angle meter type Digidrop, GBX, Roman, France.

Example 1

5

140 g ground SMA and water were charged into a double walled, oil heated reactor of 1 l, which contained a stirrer. The SMA had a MA content of 26 mole % and a molecular weight of 80000 g/mole. To this solution a 25 % NH₃ solution was added, so that the MA:NH₃ ratio was 1:1. Furthermore, a potassium salt of a SMA polymer was added having a molecular weight of 1000 g/mole and a MA content of 48 mole %. The K salt:SMA ratio was 0.03:1. Water was added until a total volume of 700 ml was obtained. The pressure was adjusted to 0.2 MPa with nitrogen. Following increasing the temperature to 160 °C, at a rotation speed of 800 rpm, the pressure raised to 0.8 MPa. After 6 hours of reaction time a polymer dispersion was obtained having a solid content of approximately 20 wt. %, the particle size being between 80 and 120 nm. The MA had been completely converted to imide. The Tg of the polymer after completion of the imidization was found to be between 190 and 200°C. The dispersion had a pH of 6.8. The contact angle of the dispersion when applied to paper was found to be smaller than 40°.

20

Example 2

140 g ground SMA and water were charged into a double walled, oil heated reactor of 1 l, which contained a stirrer. The SMA had a MA content of 26 mole % and a molecular weight of 80000 g/mole. To this solution a 25 % NH₃ solution was added, so that the MA:NH₃ ratio was 1:1. Water was added until a total volume of 700 ml was obtained. The pressure was adjusted to 0.2 MPa with nitrogen. Following increasing the temperature to 160 °C, at a rotation speed of 800 rpm, the pressure raised to 0.8 MPa. After 6 hours of reaction time a polymer dispersion was obtained having a solid content of approximately 20 wt. %, the particle size being between 80 and 120 nm. The MA had been completely converted to imide. The Tg of the polymer after completion of the imidization was found to be between 190 and 200°C. The dispersion had a pH of 7.0. The contact angle of the dispersion when applied to paper was found to be smaller than 40°.

30

Example 3

245 g ground SMA and water were charged into a double walled, oil heated reactor of 1 l, which contained a stirrer, to which 0.2 g of Surfinol 420 of Air Products was added. The SMA had a MA content of 26 mole % and a molecular weight of 80000 g/mole. To this solution a 25% NH₃ solution was added, so that the MA:NH₃ ratio was 1:1. Furthermore, a potassium salt of a SMA polymer was added having a molecular weight of 1000 g/mole and a MA content of 48 mole %. The K salt:SMA ratio was 0.03:1. Water was added until a total volume of 700 ml was obtained. Following increasing the temperature to 160 °C, at a rotation speed of 800 rpm, the pressure raised to 0.6 MPa. After 6 hours of reaction time a polymer dispersion was obtained having a solid content of approximately 35 wt. %, the particle size being between 80 and 120 nm. The MA had been completely converted to imide. The Tg of the polymer after completion of the imidization was found to be between 190 and 200°C. The dispersion had a pH of 6.9. Upon drying of the coating no film formation was observed. The contact angle of the dispersion when applied to paper was found to be smaller than 40°.

Example 4

An experiment was carried out on pilot scale, by dissolving 60 kg of ground SMA type Stapron 28110 (DSM, The Netherlands) in 99 kg of water in a pilot reactor at room temperature, to which 0.02 kg of Surfinol 420 of Air Products was added. The SMA had a MA content of 28 mole % and a molecular weight of 110000 g/mole. To this solution 11.70 kg of a 25% NH₃ solution in water was added, so that the MA:NH₃ ratio was 1:1. When admitting the NH₃ solution, the temperature was increased to approximately 78°C. The reactor was further heated until the reaction mixture had a temperature of approximately 155°C. In the course of the reaction, the reaction mixture was stirred using a motor of 35 kW with a reduction of 56 rpm. The electric power needed to drive the stirrer was recorded as a function of time. The results are summarised in Table 1. It was observed that as soon as the reaction mixture obtained a temperature of approximately 134°C, the viscosity increased significantly and a first gel was formed, indicating that the

imidization reaction was started by formation of the amide compounds. When continuing the reaction, the reaction mixture became visco-elastic, indicating the formation of the imide was taking place. Formation of SMI particles was observed after a reaction time of approximately 210 minutes, at the moment a significant decreasing viscosity was observed. It was further observed that as soon the pH of the reaction mixture obtained a value of approximately 7, the imidization was complete. After a reaction time of approximately 4 h and 15 min, heating was stopped and the reaction mixture was cooled down to room temperature. A dispersion of SMI in water was obtained having a solids content of 40 wt. %, a pH of 7, a mean particle diameter of 86 nm.

Table 1.

Reaction time (min)	Reaction temperature (°C)	Electric power (Ampère)	Rpm	Pressure (bar)	Observations
0	23	2	25	0.50	Introduction of water and Stapron
15	78	4	35	0.50	Introduction of NH ₃ solution – closing reactor
30	134	25	37	0.70	Increasing viscosity, vortex decrease
45	140	30	46	1.00	Idem
60	143	40	50	1.10	No vortex – high viscosity
75	150	50	50	1.15	Idem
90	154	50	50	1.15	Increase visco elasticity
105	158	55	50	1.80	Idem
120	157	58	50	2.00	High gloss – jelly aspect
135	156	63	50	2.00	Maximum shear resistance
150	155	63	50	2.70	Maximum shear resistance
165	155	54	50	3.00	Decreasing viscosity
180	155	48	50	3.30	Idem
195	155	38	50	3.40	Vortex coming back
210	155	29	25	3.40	Pressure increased 1 bar manually
225	155	18	20	3.50	Stop heating – start cooling
240	100	2	20	3.70	Less foam – viscosity like water
255	45	2	15	3.80	Dispersion – end of process

Example 5

The procedure of Example 4 was repeated, this time dissolving 1400 kg of ground SMA type Stapron 26080 (DSM, The Netherlands) in 2352 kg of water in a pilot reactor at room temperature, to which 0.05 kg of Surfinol 420 of Air Products was added. The SMA had a MA content of 26 mole % and a molecular weight of 80000 g/mole. To this solution 249 kg of a 25% NH_3 solution in water was added, so that the MA: NH_3 ratio was 1:1. When admitting the NH_3 solution, the temperature was increased to approximately 86°C. The reactor was further heated until the reaction mixture had a temperature of approximately 150°C. The electric power needed to drive the stirrer stirring the reaction mixture was recorded as a function of time. The results are summarised in Table 2. It was observed that as soon as the reaction mixture obtained a temperature of approximately 101°C, the viscosity increased significantly and a first gel was formed, indicating that the imidization reaction was started by formation of the amide compounds. When continuing the reaction, the reaction mixture became visco-elastic, indicating the formation of the imide was taking place. Formation of SMI particles was observed after a reaction time of approximately 5 hours, at that moment a decreasing viscosity was observed. It was further observed that as soon the pH of the reaction mixture obtained a value of approximately 7, the imidization was complete. After a reaction time of approximately 6 h and 45 min, heating was stopped and the reaction mixture was cooled down to room temperature. A dispersion of SMI in water was obtained having a solids content of 40 wt. %, a pH of 7, a mean particle diameter of 72 nm.

Table 2.

Reaction Time (min)	Reaction temperature (°C)	Electric power (Ampère)	Rpm	Pressure (bar)	Observations
0	23	2	50	0.50	Introduction of H ₂ O
15	75	4	35	0.50	Introduction of Stapron 26080*
60	86	7	37	0.70	Introduction of 25% NH ₃
75	101	10	46	1.00	Start of increase of viscosity
90	108	15	50	1.10	Strong viscosity increase
105	114	15	50	1.15	Idem
120	116	15	50	1.15	Idem
135	118	17	50	1.80	Idem
150	122	17	50	2.00	Idem
165	124	17	50	2.00	Increase of visco elasticity
180	127	22	50	2.70	Decrease of vortex
195	131	22	50	3.00	High gloss and jelly aspect
210	135	22	50	3.30	Slow movement of gel phase in the reactor
225	137	24	50	3.40	No vortex
240	138	24	50	3.40	No vortex
255	140	24	50	3.50	No vortex
270	141	35	50	3.70	No vortex
285	142	35	50	3.80	Forming of chewing gum bubbles
300	144	35	50	3.80	Idem
315	145	38	50	3.80	Idem
330	146	39	50	3.80	Idem
345	147	40	50	3.80	Idem
360	149	42	50	4.00	Very high shear resistance
375	150	43	50	5.00	Maximum sheer resistance
390	150	43	50	5.00	Maximum sheer resistance
405	149	43	50	5.00	Maximum sheer resistance
420	149	40	50	5.00	Viscosity decrease
435	150	39	50	5.00	Viscosity decrease
450	150	36	50	5.00	Light foam and vortex forming
465	153	32	25	5.00	Strong foam forming
480	154	22	25	6.00	Manuel addition of +1 bar pressure
495	154	12	25	6.00	Decrease of foam forming till 6 bar
510	155	8	25	6.00	Low viscosity and minimum foam
525	155	7	25	6.00	Stop the heating and start cooling
540	100	5	25	6.00	Less foam and viscosity like water
555	40	2	25	6.00	Dispersion – end of process

Example 6

5 The experiment of Example 1 was repeated using SMA type 2000 (from Atofina, France). The resulting dispersion had a solid content of approximately 20 wt% and a pH of 7.1. The particle size was 1500 nm.

Example 7

10 Approximately 3 kg of the product obtained from Example 5 was subjected to ultrafiltration using a Valmet Flootek CR 200/1 with a 30000 Dalton cut-off. The final stable dispersion had a 58,6% solid content.

Example 8

15 Wood free paper with dry weight of 67 g/m² was coated with an on-line film press at a speed of 1300 m/min with base coating of 5 g/m² on both paper sides calculated as dry matter. The applied coating had a solid content of 60 wt. % and contained 100 parts calcium carbonate, 8 parts latex and 8 parts starch. On top of
20 the base coating, an mid coating of 13 g/m² calculated as dry matter was applied off-line on both paper sides having the same composition as the base coating, however with a solids content of 64 wt. %.

25 The thus pre-treated paper was coated on both sides with a top coating of 6 g/m² calculated as dry matter. The top coating had the following composition: 75 parts of CaCO₃, 25 parts of kaolin, 14 parts of latex, the usual additives and 10 parts of the polymer dispersion of this invention, the properties of which are given in Table 3 below.

30 The paper was passed through a calendar having 9 successive nip passages, at a nip pressure of 220 N/m.

The thus obtained paper had a total dry weight of 115 g/m².

Comparative example

The experiment of Example 8 was repeated, however this time using as a top coat a reference coating containing 75 parts of CaCO_3 , 25 parts of kaolin, 14 parts of latex and the usual additives. The reference coating did not contain the polymer dispersion of this invention. Thereafter the paper was passed through a calendar having 11 successive nip passages, at a pressure of 280N/m at each nip.

The thus obtained paper had also a total dry weight of 115 g/m² as the dry weight of the base paper and the amount of coatings was the same as in Example 8.

Table 3

Dispersion ¹⁾	Particle size (nm)	Paper gloss
26080	80	77
28110	95	75
33003	1500	57
34080	150	73
Comp. Ex.		75

1) SMA notation, first two numbers denote the MA content, last three numbers Mw $\times 10^{-3}$.

From the comparison of the results of Example 8 with the Comparative example it becomes clear that with the polymer dispersion of this invention a similar gloss can be obtained although both the number of calander nips and the nip pressure used is lower.

It was further observed that the paper obtained according to this invention was thicker and had higher Scott Bond values as compared to the paper obtained with the Comparative example. This is attributed to the fact that with the invention the number of nips required in the calendaring process may be reduced as well as the

nip pressure, as a consequence of which the paper strength is less affected during calendaring and a high initial gloss may be obtained.

Claims

1. An aqueous polymer dispersion comprising a copolymer of anhydride monomer units and vinyl monomer units, which copolymer has been subjected to an imidization reaction, characterised in that at least 90 mole % of the anhydride monomer units of the copolymer are imidized.
2. An aqueous dispersion as claimed in claim 1, characterised in that the anhydride monomer content of the copolymer ranges between 5-50 mole %, preferably 5-29 mole % and the vinyl monomer content of the copolymer ranges between 95-50 mole %, preferably 95-81 mole %.
3. An aqueous dispersion as claimed in claims 1 or 2, characterised in that the copolymer has a molecular weight ranging between 1000-500000 g/mole, preferably between 10000-300000 g/mole, more preferably between 60000-150000 g/mole.
4. An aqueous dispersion as claimed in any one of claims 1-3, characterised in that the copolymer is a copolymer composition comprising a plurality of copolymers having varying molecular weights.
5. An aqueous dispersion as claimed in any one of claims 1-4, characterised in that the dispersion has a solid content of more than 20 wt. %, preferably more than 30 wt. %, more preferably more than 40 wt. %.
6. An aqueous dispersion as claimed in any one of claims 1-5, characterised in that the polymer dispersion comprises discrete particles having a particle size between approximately 30-400 nm, preferably between 30-120 nm.
7. An aqueous dispersion as claimed in claim 1, characterised in that the copolymer contains maleic anhydride monomer units and styrene monomer units.
8. A method for the production of an aqueous polymer dispersion comprising the steps of

- 1) reacting a starting copolymer of anhydride monomer units and a vinyl monomer units in an aqueous solution of NH_3 or an amine RNH_2 ,
- 2) subjecting the thus obtained mixture to an imidization reaction,

5

characterised in that the imidization reaction is carried out under reaction conditions which are selected so that at least 90 mole % of the anhydride monomer units have been imidized.

10

9. A method as claimed in claim 8, characterised in that the imidization reaction is continued until a degree of imidization of the copolymer of at least 95 mole %, preferably virtually complete imidization, is obtained.

15

10. A method as claimed in claim 8 or 9, characterised in that the imidization reaction is carried out in the presence of an alkali salt of an acid functional polymer containing acid functional monomer units and vinyl aromatic monomer units, preferably alkali salt of styrene maleic anhydride copolymer.

20

11. A method as claimed in any one of claims 8-10, characterised in that the copolymer has a molecular weight ranging between 1000-500000 g/mole, preferably between 10000-300000 g/mole, more preferably between 60000-150000 g/mole.

25

12. A method as claimed in any one of claims 8-11, characterised in that NH_3 or RNH_2 is added in such an amount that the ratio NH_3 or amine : anhydride monomer in the starting copolymer is between 0.5-10:1.

30

13. A method as claimed in any one of claims 8-12, characterised in that the molar ratio between the amine or NH_3 and the anhydride monomer in the copolymer ranges between 1.2-0.8:1, preferably slightly under the equimolar ratio.

14. A method as claimed in any one of claims 8-13, characterised in that in the course of the imidization reaction, the reaction mixture is stirred so as to minimise adhesion of the reaction mixture to the reactor wall.

15. A method as claimed in any one of claims 8-14, characterised in that the imidization reaction is carried out at a temperature above 100°C, preferably between 120-195°C, more preferably at a temperature between 150-175°C.

5

16. An aqueous coating composition for coating a product to be imprinted, characterised in that the coating composition contains a polymer dispersion as claimed in any one of claims 1-7 or a polymer dispersion obtained with the method of any one of claims 8-15.

10

17. An aqueous coating composition according to claim 16, further containing binders, conventional pigments and, optionally, additives.

15

18. Use of a polymer dispersion as claimed in any one of claims 1-7 or a polymer dispersion obtained with the method of any one of claims 8-15 for coating a surface to be imprinted.

20

19. Use as claimed in claim 18, characterised in that the surface is paper, paperboard, cardboard, organic film e.g. polyethylene film, metal or textile.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/03/00731

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F8/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 43 42 157 A (LEUNA-WERKE GMBH) 14 June 1995 (1995-06-14) page 2, line 32 -page 3, line 27; claims 1-9	1-19
X	US 4 588 786 A (H. KADONO) 13 May 1986 (1986-05-13) the whole document	1-19
A	US 6 232 405 B1 (J. C. SCHMIDHAUSER) 15 May 2001 (2001-05-15) claims 1-10	1
A	WO 99 45039 A (DSM N.V.) 10 September 1999 (1999-09-10) page 3, line 23 -page 5, line 4; claims 1-12	1

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 February 2004

Date of mailing of the international search report

10/02/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Permentier, W

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 4342157	A	14-06-1995	DE 4342157 A1	14-06-1995
US 4588786	A	13-05-1986	JP 1825418 C	28-02-1994
			JP 5032402 B	17-05-1993
			JP 60079012 A	04-05-1985
US 6232405	B1	15-05-2001	CA 2331082 A1	02-08-2001
			EP 1122263 A1	08-08-2001
WO 9945039	A	10-09-1999	NL 1008469 C2	07-09-1999
			AU 2860699 A	20-09-1999
			BR 9908462 A	14-11-2000
			EP 1060197 A1	20-12-2000
			JP 2002505351 T	19-02-2002
			WO 9945039 A1	10-09-1999
			US 6407197 B1	18-06-2002

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

☐ BLACK BORDERS

☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES

☐ FADED TEXT OR DRAWING

☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING

☐ SKEWED/SLANTED IMAGES

☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS

☐ GRAY SCALE DOCUMENTS

☐ LINES OR MARKS ON ORIGINAL DOCUMENT

☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY

☒ OTHER: hole punched over text

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.